

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 September 2002 (26.09.2002)

PCT

(10) International Publication Number
WO 02/074421 A1

(51) International Patent Classification⁷: **B01D 53/22**,
71/02, 63/06

(21) International Application Number: PCT/GB02/01079

(22) International Filing Date: 18 March 2002 (18.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0106478.1 16 March 2001 (16.03.2001) GB

(71) Applicant (for all designated States except US): **THE ROBERT GORDON UNIVERSITY** [GB/GB]; Schoolhill, Aberdeen AB10 1FR (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **GOBINA, Edward** [GB/GB]; The Robert Gordon University, Schoolhill, Aberdeen AB10 1FR (GB).

(74) Agent: **MURGITROYD & COMPANY**; Scotland House, 165-169 Scotland Street, Glasgow G5 8PL (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

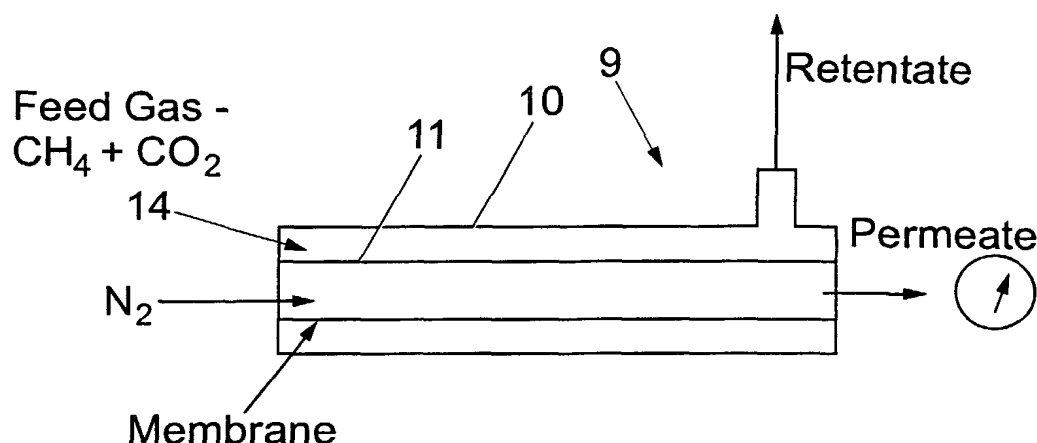
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: APPARATUS AND METHOD FOR SEPARATING GASES



(57) Abstract: An apparatus and method to separate a mixture of gases - such as carbon dioxide and methane - by means of an inorganic membrane comprising a ceramic support and a silica layer. The invention can efficiently separate the gaseous mixture and can also cope with the extreme conditions found in e.g. hydrocarbon producing wells. A method of manufacturing the apparatus is also disclosed.



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1 APPARATUS AND METHOD FOR SEPARATING GASES

2
3 This invention relates to an apparatus and method for
4 separating gases and in particular an apparatus
5 comprising inorganic membranes for removing acidic gases
6 from natural gas.

7
8 Natural gas reserves known to contain a relatively high
9 content of nitrogen, carbon dioxide or hydrogen sulphide
10 are rarely recovered due to the costs incurred to purify
11 the gas mixture.

12
13 Impure methane is also commonly produced by landfill
14 sites but its commercial exploitation is generally
15 prohibited by the costs associated with purifying it.

16
17 Current processing systems are generally regarded to be
18 uneconomical above 1.5% levels of carbon dioxide. To
19 remove carbon dioxide from natural gas, chemical scrubs
20 are commonly used. This results in a significant amount
21 of waste product which must be suitably disposed of,
22 adding further costs to remove the carbon dioxide.

1 Moreover, the mechanical equipment used with such
2 chemical scrubs is susceptible to failure.

3
4 According to a first aspect of the present invention,
5 there is provided an apparatus to separate at least one
6 first gas from a mixture comprising the at least one
7 first gas and at least one second gas, the apparatus
8 comprising a membrane adapted to permit passage of the at
9 least one first gas therethrough whilst substantially
10 preventing passage of the at least one second gas
11 therethrough.

12
13 Preferably, the membrane is an inorganic membrane.

14
15 The first gas may be water vapour, nitrogen or preferably
16 carbon dioxide.

17
18 Preferably, the apparatus separates a gas mixture
19 comprising natural gas and an acidic gas, and typically, the
20 acidic gas is the first gas and the natural gas is the
21 second gas.

22
23 The acidic gas in preferred embodiments is carbon dioxide
24 although other acidic gases such as hydrogen sulphide,
25 may be the first gas.

26
27 Preferably, the inorganic membrane is formed such that it
28 maximises the contact of the gaseous mixture with the
29 surface of the inorganic membrane. Preferably, the
30 inorganic membrane is provided as a tube comprising a
31 bore. Optionally, a series of tubes may be used, and the
32 tube may be corrugated or coiled. The gaseous mixture may

1 be directed through the bore of the tubes and separated
2 according to the present invention.

3

4 More preferably, each tube is an inner tube provided
5 within an impermeable second outer tube. Preferably, the
6 gaseous mixture is injected into the annulus between each
7 pair of outer and inner tubes.

8 Preferably, a graphite seal mounts each inner tube in
9 each outer tube.

10

11 Preferably, the inorganic membrane comprises a means to
12 control the type of gaseous molecules passing
13 therethrough. Preferably the outer diameter of the inner
14 tubes is between 5-12mm, more preferably 10mm.

15 Preferably the thickness of the inner tubes is between
16 1.5 and 2mm, more preferably 1.7mm. There may be any
17 number of inner tubes although preferably there are
18 between 10 and 50 inner tubes depending on the flow rate
19 and the purity of the gaseous mixture. Preferably, the
20 inner tubes are approximately 1 metre in length.

21

22 Preferably, the inorganic membrane comprises a plurality
23 of chemically discreet portions. Preferably, a first
24 portion is a separating layer. Preferably, a second
25 portion is a support.

26

27 Preferably, the separating layer comprises a layer
28 adapted to allow passage of the at least one first gas
29 through the membrane and resist passage of the at least
30 one second gas through the membrane.

31

32 Preferably, the separating layer comprises any one of, a
33 combination of, or all of; silica, magnesium oxide, gamma

1 alumina or a molecular sieve. Preferably, the molecular
2 sieve is a carbon molecular sieve.

3

4 The support may comprise alpha alumina, stainless steel,
5 carbon or any other suitable inorganic material.

6

7 Preferably, the separating layer is provided on a surface
8 of the support, and where the support is a tube, the
9 separating layer may be provided on a surface of the
10 inner bore of the tube.

11

12 The layer(s) of the separating layer may be provided in
13 any order although in preferred embodiments, a layer of
14 gamma alumina is first added to the support. Typically,
15 a layer of silica is then added on top of the layer of
16 gamma-alumina. Optionally, a molecular sieve may be
17 added as a further layer.

18

19 More preferably, the separating layer has a chemical
20 affinity for the at least one first gas. A group II
21 metal oxide, preferably magnesium oxide, may be added,
22 optionally in place of the silica and molecular sieve, to
23 increase the chemical affinity of the at least one first
24 gas towards the membrane.

25

26 According to a second aspect of the present invention,
27 there is provided an apparatus to separate at least one
28 first gas from a mixture comprising the at least one
29 first gas and at least one second gas, the apparatus
30 comprising a first tube and a second tube, the first tube
31 comprising a membrane adapted to permit passage of the at
32 least one first gas therethrough whilst substantially
33 preventing passage of the at least one second gas

1 therethrough, the first tube being mounted substantially
2 within the second tube and being sealed therein by a
3 graphite seal.

4

5 Preferably, the membrane is the membrane according to the
6 first aspect of the invention.

7

8 According to a third aspect to the present invention,
9 there is provided a method of manufacturing apparatus to
10 separate at least one first gas from a mixture comprising
11 the at least one first gas and at least one second gas,
12 the apparatus comprising an membrane adapted to permit
13 passage of the at least one first gas therethrough whilst
14 substantially preventing passage of the at least one
15 second gas therethrough, the method comprising-

16

17 providing a support;
18 immersing the support in a sol;
19 removing the support from the sol; and
20 allowing the support to dry.

21

22 Preferably, the membrane is an inorganic membrane.

23

24 Preferably, the support is a ceramic support.

25

26 Preferably, the membrane manufactured according to the
27 second aspect of the invention is the membrane provided
28 according to the first aspect of the invention.

29

30 Preferably, the following steps of the method-

31 immersing the support in a sol;
32 removing the support from the sol; and
33 allowing the support to dry;

1 are repeated at least once. More preferably, said steps
2 of the method are repeated twice.

3

4 Preferably, the sol is in the liquid state and forms at
5 least a portion of the separating layer. Preferably, the
6 sol coats the support. Preferably, the sol forms at least
7 a part of the separating layer.

8

9 Preferably, the support is dried by applying heat.

10

11 In certain embodiments, the method may be repeated to
12 coat the support with a second sol.

13

14 Optionally, the support may be coated with a molecular
15 sieve, preferably a carbon molecular sieve, instead of,
16 although preferably, in addition to, other sols. In such
17 embodiments carbonisation is preferably affected by
18 heating the support with the carbon molecular sieve in an
19 argon atmosphere.

20

21 According to a fourth aspect of the present invention,
22 there is provided a method to separate at least one first
23 gas from a mixture comprising the at least one first gas
24 and at least one second gas, the method comprising the
25 steps of

26 bringing the said mixture into contact with a
27 membrane;

28 allowing passage of the at least one first gas
29 through the membrane whilst substantially preventing
30 passage of the at least one second gas through the
31 membrane.

32

33 Preferably, the membrane is an inorganic membrane.

1

2 Preferably, the method according to the third aspect of
3 the invention is used in conjunction with the apparatus
4 according to the first aspect of the invention.

5

6 In certain embodiments of the invention, the method is
7 performed in a downhole environment.

8

9 Typically, the at least one first gas includes an acidic
10 gas. Preferably, the at least one first gas includes
11 carbon dioxide. More preferably, the at least one first
12 gas and the at least one second gas may be recovered,
13 suitable for use with alternative applications.

14

15 Typically, the at least one second gas includes a
16 hydrocarbon gas. Preferably, the at least one second gas
17 includes methane. Preferably, the said mixture is
18 essentially a mixture of methane and carbon dioxide.

19

20 Alternatively, the apparatus and method may be used to
21 remove carbon dioxide from nitrogen. The apparatus and
22 method according to any aspect of the invention may also
23 be used to separate other gas, fluid, or liquid mixtures,
24 for example, to remove hydrogen sulphide from methane.

25

26 Embodiments of the present invention will now be
27 described by way of example only, with reference to the
28 following diagram, wherein:-

29

Fig. 1a is a side view of an inorganic membrane
30 according to the present invention;

31

Fig. 1b is an enlarged side view of the inorganic
32 membrane according to the present invention; and,

1 Fig. 2 is a diagrammatic view of a tube comprising
2 the inorganic membrane;
3 Fig. 3 is a graph showing the recovery and
4 separation factor for an inorganic membrane in
5 accordance with the present invention for different
6 concentrations of carbon dioxide in a feed gas;
7 Fig. 4 is a graph showing the effect of deposition
8 time on thickness of a silica membrane in accordance
9 with the present invention;
10 Fig. 5 is a schematic view of an inorganic membrane
11 in accordance with the present invention showing the
12 permeation or retention of various molecules;
13 Fig. 6a is a first electron micrograph output
14 showing the structure of an inorganic membrane in
15 accordance with the present invention at a
16 magnification of 2,500;
17 Fig. 6b is a second electron micrograph output of
18 the inorganic membrane at a magnification of 1,000.
19 Fig. 7 is a side view of a tube comprising the
20 inorganic membrane.

21

22 Example 1

23

24 Figs. 1a and 1b show an inorganic membrane 1 in
25 accordance with the present invention. In summary, the
26 membrane 1 is used to remove carbon dioxide CO₂ from a
27 gaseous mixture comprising methane CH₄ and carbon dioxide
28 CO₂ in accordance with the present invention. The
29 inorganic membrane 1 comprises a relatively highly porous
30 ceramic support 2 and a separation layer 3.

31

32 The support 2 is a coarse porous support, and this first
33 preferred example of support 2 comprises 76% alpha-

1 alumina and 23% titania, the support 2 typically having a
2 pore size of 500nm and a porosity of 45%. Such a support
3 2 is commercially available, but hitherto has only been
4 used as a filter for microfiltration. The support 2 may
5 alternatively be made from any other suitable material,
6 for example, silicon carbide, zirconia, stainless steel
7 or carbon.

8
9 The separating layer 3 of Example 1 is a layer of silica
10 3.

11
12 The membrane 1 is prepared by a repeated dip-coating
13 technique. The support 2 is repeatedly dipped into a
14 precursor or "sol" (not shown) and dried to form an
15 evaporated layer of sol on the support 2, thereby forming
16 the membrane 1.

17
18 The sol is prepared by mixing nine parts of isopentane
19 and one part silicon elastomer, to obtain a clear and
20 colourless sol. A curing agent such as one from the
21 Sylgard® series is then added equivalent to one-tenth of
22 the elastomer and the resulting sol mixed at room
23 temperature.

24
25 The sol is permitted to age over a period of 5-30 minutes
26 (most preferably 20 minutes), and thereafter, the support
27 2 is immersed into the aged sol for approximately 20
28 minutes. The sol is then drained and evaporated from the
29 support 2 by drying the support 2 at 65°C for 24 hours in
30 an oven to form a layer on the support 2. The procedure
31 is repeated a number of times until the layer is of the
32 required thickness, normally between 1-12 μ m, preferably 6

1 μm . Fig. 4 shows the membrane thickness in relation to
2 deposition time and No. of dips.

3

4 When a CO_2 molecule collides with the separation layer 3
5 of the inorganic membrane 1, it may be adsorbed into the
6 separation layer 3 and proceed through the pores 5 in the
7 support 2. The CO_2 molecule continues through the
8 support 2 and is recovered along with other CO_2 molecules
9 by any suitable means.

10

11 In contrast, when a CH_4 molecule collides with the
12 separation layer 3 of the inorganic membrane 1, it is
13 unlikely to be adsorbed into the separation layer 3 and
14 will instead continue through the bore of the tube of the
15 inorganic membrane 1 where it may be collected along with
16 other CH_4 molecules. Generally, CH_4 molecules form bonds
17 with the separation layer 3 less readily than CO_2
18 molecules.

19

20 Carbon dioxide is currently injected downhole to increase
21 the rate of recovery of production fluids from
22 reservoirs. The present invention therefore provides a
23 means to obtain carbon dioxide proximate to where it may
24 be used. A continuous loop is thus formed in which
25 carbon dioxide is recovered from the natural gas and may
26 be utilised to recover further production fluids. Indeed
27 the CO_2 may never need to be transported to the surface
28 as it may be transported from the membrane 1 to the
29 reinjection point which saves on further time and cost.

30

31 The inorganic membrane may be formed as a flat sheet or
32 preferably, in thin tubes having an inner diameter of,
33 for example 3-11mm and an outer diameter of for example

1 5-12mm. The gaseous mixture 4 is directed through the
2 inner bore of this tube membrane 1. Such tubes may be
3 coiled or corrugated to increase the number of collisions
4 between the molecules in the gaseous mixture 4 and the
5 inner surface of the inorganic membrane 1.

6
7 An example of the tube arrangement suitable for use in
8 accordance with the present invention is shown in Fig. 7.
9 A tubular stainless steel vessel 9 comprises an inner
10 tube 11, inlet ports 13, 17 and a seal 12. The inner
11 tube 11 is made from the inorganic membrane 1 and the
12 outer tube 10 can be made from any suitable material,
13 such as stainless steel. Normally approximately 10 tubes
14 are used in any one vessel 9, although only one end 15 of
15 one tube is shown in Fig. 7. Certain embodiments of the
16 invention with high flow rates may use more than 10
17 tubes. The seal 12 is preferably made from graphite as
18 this is compressible, inert, high-temperature resistant
19 to enable permeability studies at elevated temperatures,
20 and cost effective. The second end 16 of the vessel 9 is
21 not shown in Fig. 7, but typically mirrors the
22 configuration of the first end 15.

23
24 The gaseous mixture 4 is injected through the inlet port
25 13 into the annulus 14 between the inner 11 and outer 10
26 tubes. In this example CO₂ molecules are separated from
27 CH₄ molecules, but other mixtures may be separated. The
28 mixture 4 flows through the annulus 14, the CO₂ molecules
29 selectively adsorbing in the inorganic membrane 1 which
30 forms the tube 11. The second end 16 of the inner tube 11
31 of the vessel 9 corresponds to a first outlet (not
32 shown), and the second end 16 of the annulus 14 of the
33 vessel 9 corresponds to a second outlet (not shown). The

1 relatively pure CH₄ and CO₂ are recovered separately
2 through their respective outlets. A sweep gas 18 may
3 optionally be injected through the inlet 17 of the inner
4 tube 11, to increase the flow rate of the CO₂ therein.

5

6 A simplified embodiment of the tube 11 is shown in Fig. 2
7 with like parts labelled correspondingly.

8

9 The efficiency of the membrane 1 in separating CO₂ from
10 natural gas is dependent on both the geometry in terms of
11 surface area and flow rate and the membrane 1
12 characteristics. The tests conducted to date have only
13 considered the factors relating to the membrane and not
14 optimised the geometry. Hence a standard test set up can
15 be used for all testing.

16

17 Thus the measures of selectivity and efficiency relate to
18 a staged separation factor. The tests are conducted in
19 two stages using the equipment as per Fig. 2 or Fig. 7.

20

21 In a first test, a feed gas was introduced in known CO₂
22 and CH₄ composition and mass flow rates and the permeate
23 gas is fed through a flow meter and the concentration of
24 the permeate is analysed ignoring the sweep gas. This
25 gives a measure of the staged separation factor. The
26 retentate gas is free to exhaust.

27

28 To calculate the Staged Separation Factor (SSF), the
29 following formula is used:-

30

31
$$SSF = (\text{Conc. Of CH}_4 / \text{Conc. Of CO}_2 \text{ in permeate}) / (\text{Conc.}$$

32
$$\text{Of CH}_4 / \text{Conc of CO}_2 \text{ in feed}) \times 100$$

33

1 Therefore the lower the SSF the better is the separation
2 efficiency of the separating means (in this case
3 membranes).

4
5 In the second test, a feed gas is introduced in known CO₂
6 and CH₄ composition and mass flow rates and the retentate
7 gas is fed through a flow meter and the concentration of
8 the retentate is analysed ignoring the sweep gas. This
9 gives a measure of the Staged Recovery Factor. The
10 permeate gas is free to exhaust.

11
12 The SRF is calculated using the following formula-

13
14
$$\text{SRF} = (\text{Conc. Of CH}_4 / \text{Conc. Of CO}_2 \text{ in retentate}) / (\text{Conc.}$$

15
$$\text{Of CH}_4 / \text{Conc of CO}_2 \text{ in feed}) \times 100$$

16
17 Therefore the higher the SRF, the better is the
18 efficiency of the separating means (in this case
19 membranes.) Parameters affecting separation efficiency
20 are discussed in Industrial Gas Separations, pp 132-134
21 (Schell & Houston) and Gas Purification, Membrane
22 Permeation Processes pp1242 - 1245.

23
24 SSF and SRF measurements on the present example of an
25 inorganic membrane is shown in Fig. 3.

26
27 The measurements were taken under conditions of 1
28 atmosphere and for a relatively small tube. It is
29 expected that the selectivity of separating CO₂ from CH₄
30 will increase when the pressure is increased. Moreover,
31 use of longer tubes or two - three smaller tubes in
32 series will also increase selectivity.

33

1

2 **Example 2**

3

4 An inorganic membrane 1 according to the invention
5 comprises a porous ceramic support 2 and a separation
6 layer 3, as shown in Figs. 1a and 1b.

7

8 Example 2 differs from Example 1 only in the composition
9 of separation layer 3 provided. Common features between
10 Example 1 and Example 2 are not described here for
11 example 2.

12

13 The separation layer 3 of the Example 2 comprises a
14 gamma-alumina layer (not shown) mounted on the support 2,
15 a silica layer (not shown) and a carbon molecular sieve
16 (not shown).

17

18 To form the membrane 1 of the Example 2, the support 2 is
19 exposed to a boemite sol maintained at 0.6 mol/L (as the
20 gamma alumina source) using the dip-coating technique as
21 described for example 1. The support 2 is immersed into
22 the boemite sol for approximately two minutes. The
23 membrane is then air dried overnight and heated to
24 between 700 and 800°C at a rate of 1°C/minute. The
25 process is normally repeated three times or more to
26 achieve the required thickness of gamma alumina on the
27 support 2, normally between 1-12µm, preferably 6 µm.

28

29 Once the required gamma-alumina layer thickness has been
30 added to the support 2, a silica or carbon monocular
31 sieve layer is then applied to form the final separating
32 layer 3. The silica-layer is deposited over the gamma

1 alumina by the method described above in relation to
2 Example 1.

3
4 To deposit the carbon monocular sieve layer, the
5 alumina/silica coated support 2 is dipped in a
6 polyetherimide solution of between 1 and 5mol⁻¹,
7 preferably 3mol⁻¹. The support 2 is then dried in air.
8 Carbonisation is performed in an argon atmosphere using a
9 predefined temperature profile. In this example, the
10 support was heated from 20-80°C for 2 hours and then from
11 80-120°C for 4 hours although a variety of temperature
12 profiles may be suitably employed. Such a process may be
13 repeated as necessary to achieve the required CO₂/CH₄
14 selectivity and CO₂ permeability.

15

16 **Example 3**

17

18 An inorganic membrane 1 according to the invention
19 comprises a porous ceramic support 2 and a separation
20 layer 3, as shown in Figs. 1a and 1b.

21

22 Example 3 differs from Example 1 only in the composition
23 of separation layer 3 provided. Common features between
24 Example 1 and Example 3 are not described here for
25 Example 3.

26

27 The separation layer of Example 3 does not comprise a
28 silica layer in contrast to the previous Examples 1 and
29 2. A layer of gamma-alumina is added directly onto the
30 support 2 as detailed for Example 2.

31

32 The support 2 is then chemically modified by impregnating
33 its surface using magnesium nitrate, Mg(NO₃)₂. Mg(NO₃)₂

1 reduces to form MgO which is thus located in the pores of
2 the separating layer so that the surface concentration is
3 4 mmols Mg per square metre.

4

5 The chemical affinity between the magnesium oxide and the
6 carbon dioxide increases the selectivity of the membrane
7 1.

8

9 The ceramic nature of the inorganic membrane 1 may be
10 used at high temperatures and pressures and in extreme
11 conditions, for example downhole. Moreover, the ceramic
12 materials are resistant to acidic degradation; acids such
13 as carbonic acids being commonly formed thereabouts by
14 the combination of CO₂ and H₂O. Therefore, embodiments of
15 the invention can be used to separate mixtures of 'wet'
16 gases which would degrade other separating means.
17 Ceramic materials also have a high mechanical strength.

18

19 Embodiments of the invention used downhole have the
20 advantage that acidic gases are removed before transfer
21 by pipeline thereby reducing the corrosion of the
22 pipeline caused by such acidic gases.

23 The passage of CO₂ through the membrane 1 enables
24 continuous production of a relatively pure methane at
25 high pressure making the process extremely cost
26 effective.

27

28 Most territories impose restrictions on releasing the
29 environmentally damaging CO₂ to the atmosphere and so
30 certain embodiments of the present invention provide a
31 means to remove this gas from natural gas before flaring.

32

The apparatus according to the present invention may also be used in exhaust stacks to remove, for example, CO₂ from exhaust fumes. For example, the impure methane produced from landfill sites may be purified on site and then used as a fuel.

The hybrid structures may be characterised by X-ray diffraction, scanning electron microscopy (SEM), nitrogen absorption, X-ray photoelectron spectroscopy, BET surface analysis and EDAX surface elemental analysis. SEM photographs are shown in Figs. 6a and 6b at 2500 and 1000 times magnification respectively.

Embodiments of the invention may be used to separate other gaseous or fluid mixtures, e.g. N₂ or H₂S may be separated from raw natural gas at mildly high temperatures of ~50-100°C. This is permitted by the relative molecular dimensions of CH₄, N₂, CO₂, H₂O and H₂S which are summarised in the table below

Molecule	Size Å
CH ₄	3.8
CO ₂	3.3
N ₂	3.6
H ₂ O	2.7
H ₂ S	3.6
(Membrane)	3.6-3.7Å

Thus, even though CH₄ is lighter than the other molecules and so would be expected to penetrate the membrane more readily than the heavier molecules, it has been found that membranes according to the invention allow passage

1 of the heavier molecules while restricting passage of the
2 lighter methane molecules.

3

4

5 Preferably, the selectivity of CO₂/CH₄ is 150 at 350°C;
6 that is 150 CO₂ molecules will travel through the
7 membrane for each CH₄ molecule that travels through the
8 membrane. Preferably, the selectivity of CO₂/N₂ is 120 at
9 350°C. Preferably, the permeability of CO₂ through the
10 membrane 1 is $>4 \times 10^{-7}$ mol/m²sPa at 350°C. Preferably,
11 the durability of the inorganic membrane 1 is greater
12 than 500 hours at 350°C in corrosive environments.

13

14 An advantage of using ceramic membranes to purify
15 natural gas is their durability. Absorbent performance
16 of known separating means generally decrease with their
17 age whereas the absorbent performance of ceramic
18 materials do not decrease with age. Embodiments
19 including a silica layer are particularly durable.
20 Further advantages of the use of ceramics in such
21 applications may include enhanced plant performance and a
22 reduction in energy consumption. Ceramic materials may
23 also be used for mixtures with high CO₂ concentrations
24 for example, ranging from 3% to 72% CO₂.

25

26 Improvements and modifications may be made without
27 departing from the scope of the invention.

1 **Claims**

2

3 1. An apparatus to separate at least one first gas
4 from a mixture comprising the at least one first gas
5 and at least one second gas, the apparatus
6 comprising a membrane adapted to permit passage of
7 the at least one first gas therethrough whilst
8 substantially preventing passage of the at least one
9 second gas therethrough.

10

11 2. An apparatus as claimed in claim 1, wherein the
12 membrane is a ceramic membrane.

13

14 3. An apparatus as claimed in any preceding claim,
15 wherein the first gas comprises an acidic gas and
16 the second gas comprises methane.

17

18 4. An apparatus as claimed in any preceding claim,
19 wherein the first gas comprises carbon dioxide.

20

21 5. An apparatus as claimed in any preceding claim,
22 wherein the membrane comprises at least one tube
23 having a bore.

24

25 6. An apparatus as claimed in claim 5, wherein the
26 at least one tube is corrugated or coiled.

27

28 7. An apparatus as claimed in claim 5 or 6,
29 wherein the at least one tube comprises an inner
30 tube provided within an impermeable second outer
31 tube and the mixture comprising the at least one

1 first gas and at least one second gas is injected
2 into an annulus between the inner and outer tubes.
3

4 8. Apparatus as claimed in claim 7, wherein a
5 graphite seal mounts the inner tube in the outer
6 tube.
7

8 9. Apparatus as claimed in any preceding claim,
9 wherein the membrane comprises at least one of
10 silica, magnesium oxide, gamma alumina and a
11 molecular sieve.
12

13 10. Apparatus as claimed in claim 9, wherein the
14 molecular sieve is a carbon molecular sieve.
15

16 11. Apparatus as claimed in any preceding claim,
17 wherein the membrane comprises-

18 a separating portion adapted to allow passage
19 of the at least one first gas through the membrane
20 and substantially resist passage of the at least one
21 second gas through the membrane and,
22 a support portion.
23

24 12. Apparatus as claimed in claim 11, wherein the
25 support portion comprises at least one of alpha
26 alumina, stainless steel and carbon.
27

28 13. Apparatus as claimed in claim 11 or claim 12,
29 wherein the separating portion is provided on a
30 surface of the support.
31

1 14. Apparatus as claimed in claim 13, wherein the
2 separating portion comprises a layer of gamma
3 alumina and a layer of silica.
4

5 15. Apparatus as claimed in claim 14 when dependent
6 upon any of claims 11 to 13, wherein the layer of
7 gamma alumina is provided on the support portion and
8 the layer of silica is provided on the layer of
9 gamma alumina.
10

11 16. Apparatus as claimed in any of claims 11 to 15,
12 wherein the separating portion has a chemical
13 affinity for the at least one first gas.
14

15 17. Apparatus as claimed in any preceding claim,
16 wherein a group II metal oxide is added to the
17 membrane to increase the chemical affinity of the at
18 least one first gas toward the membrane.
19

20 18. Apparatus as claimed in claim 17, wherein the
21 group II metal oxide is magnesium oxide.
22

23 19. A method of manufacturing apparatus as claimed
24 in any preceding claim, the method comprising-
25

26 providing a support;
27 immersing the support in a sol;
28 removing the support from the sol; and
29 allowing the support to dry.
30

31 20. A method as claimed in claim 19, wherein the
32 following steps of the method-

1 immersing the support in a sol;
2 removing the support from the sol; and
3 allowing the support to dry;
4 are repeated at least once.

5

6 21. A method as claimed in any one of claims 19 or
7 20 when dependent upon any of claims 11 to 16,
8 wherein the sol forms at least part of the
9 separating portion.

10

11 22. A method as claimed in any one of claims 19 to
12 21, wherein the support is dried by applying heat.

13

14 23. A method as claimed in any one of claims 19 to
15 22 which is repeated to coat the support with a
16 second sol.

17

18 24. A method as claimed in any of claims 19 to 23
19 when dependent on claim 10, wherein carbonisation is
20 affected by heating the support with the carbon
21 molecular sieve in an argon atmosphere.

22

23 25. A method to separate at least one first gas
24 from a mixture comprising the at least one first gas
25 and at least one second gas, the method comprising
26 the steps of

27 bringing the said mixture into contact with a
28 membrane;

29 such that the at least one first gas passes
30 through the membrane whilst passage of the at least
31 one second gas through the membrane is substantially
32 prevented.

1 26. A method as claimed in claim 25, wherein the
2 membrane is an inorganic membrane.

3

4 27. A method as claimed in claim 25 or claim 26,
5 which is performed in a downhole environment.

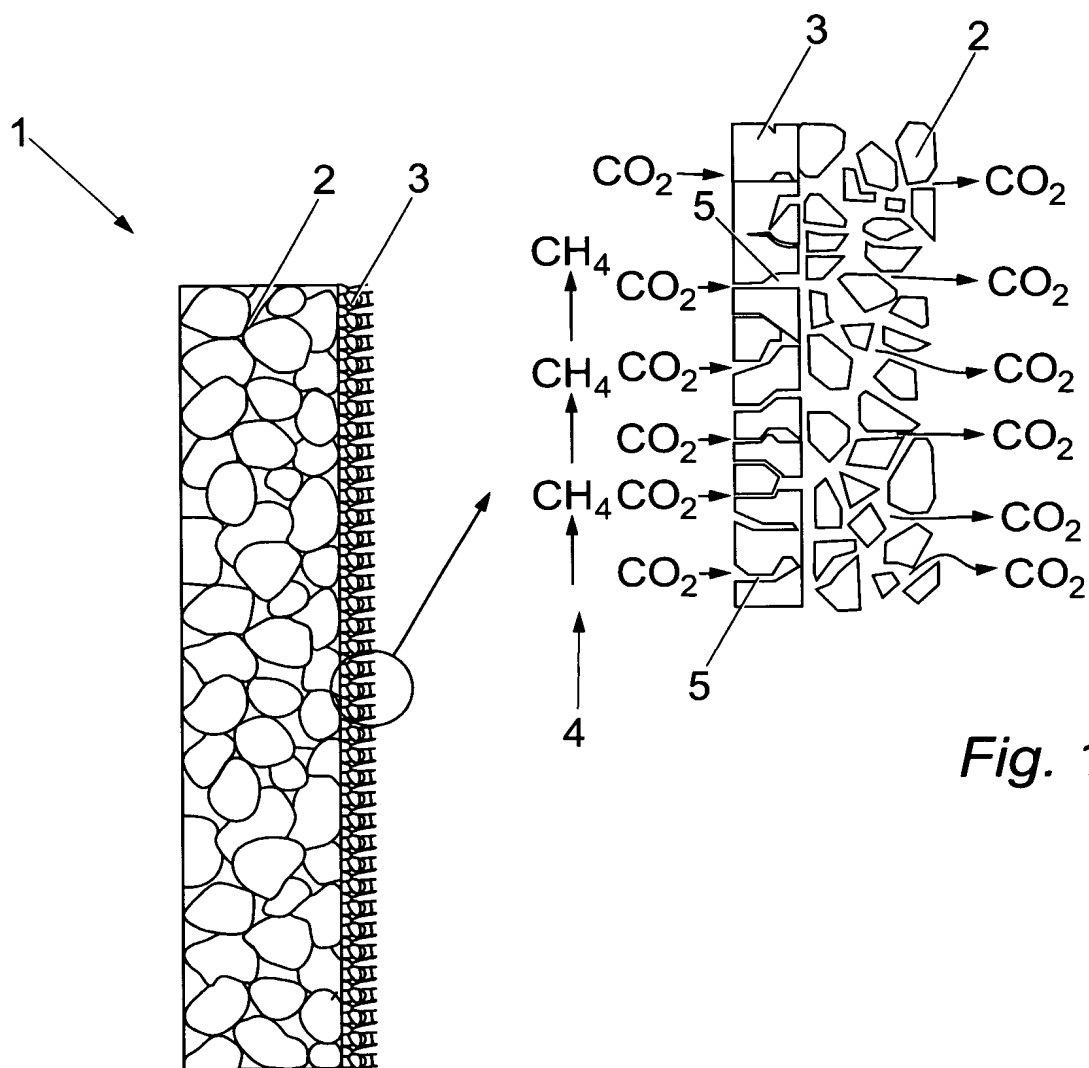
6

7 28. A method as claimed in any one of claims 25 to
8 27, wherein the at least one first gas and the at
9 least one second gas are recovered for subsequent
10 use.

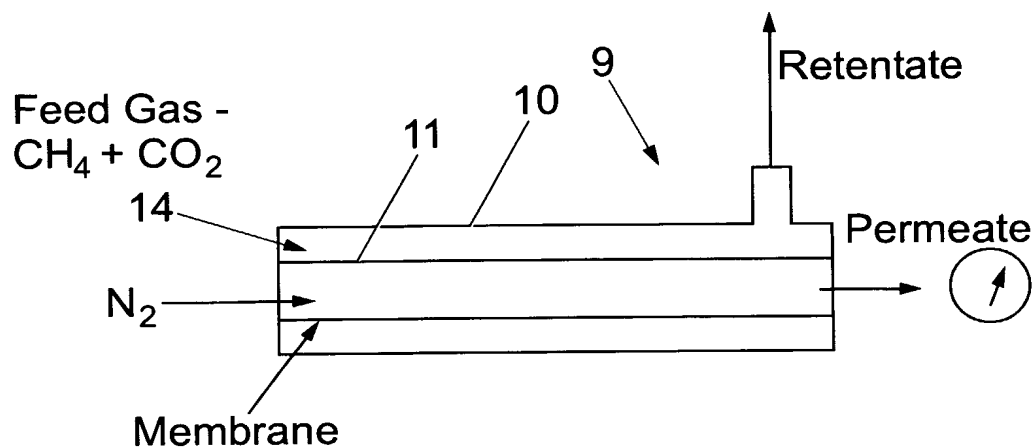
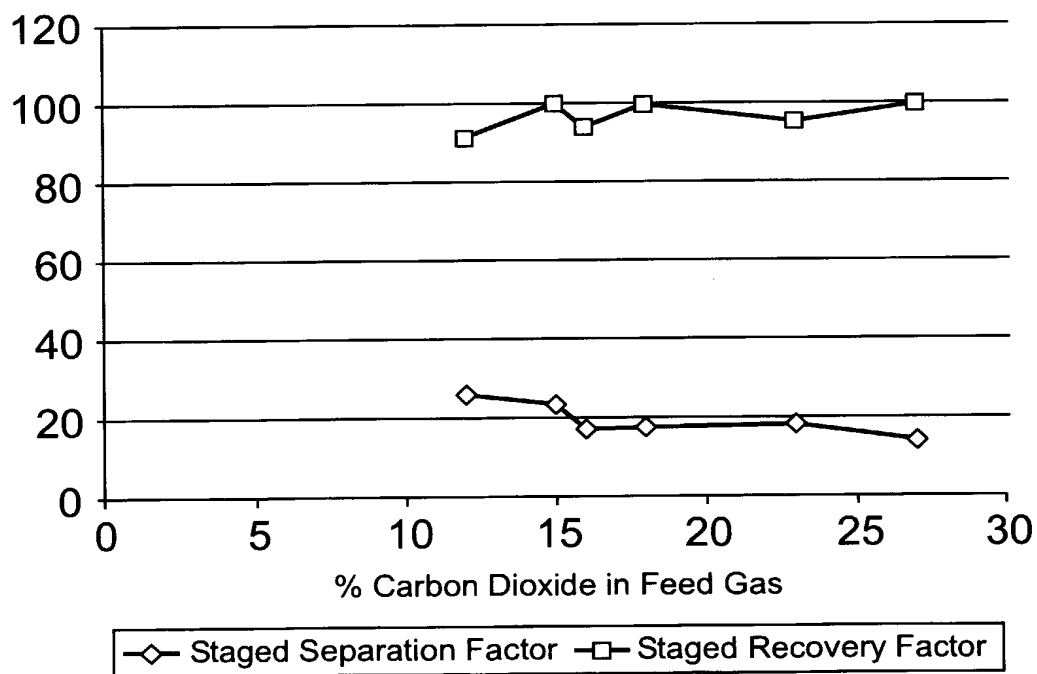
11

12 29. An apparatus to separate at least one first gas
13 from a mixture comprising the at least one first gas
14 and at least one second gas, the apparatus
15 comprising a first tube and a second tube, the first
16 tube comprising a membrane adapted to permit passage
17 of the at least one first gas therethrough whilst
18 substantially preventing passage of the at least one
19 second gas therethrough, the first tube being
20 mounted substantially within the second tube and
21 being sealed therein by a graphite seal.

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*Fig. 1a**Fig. 1b*

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*Fig. 2**Fig. 3*

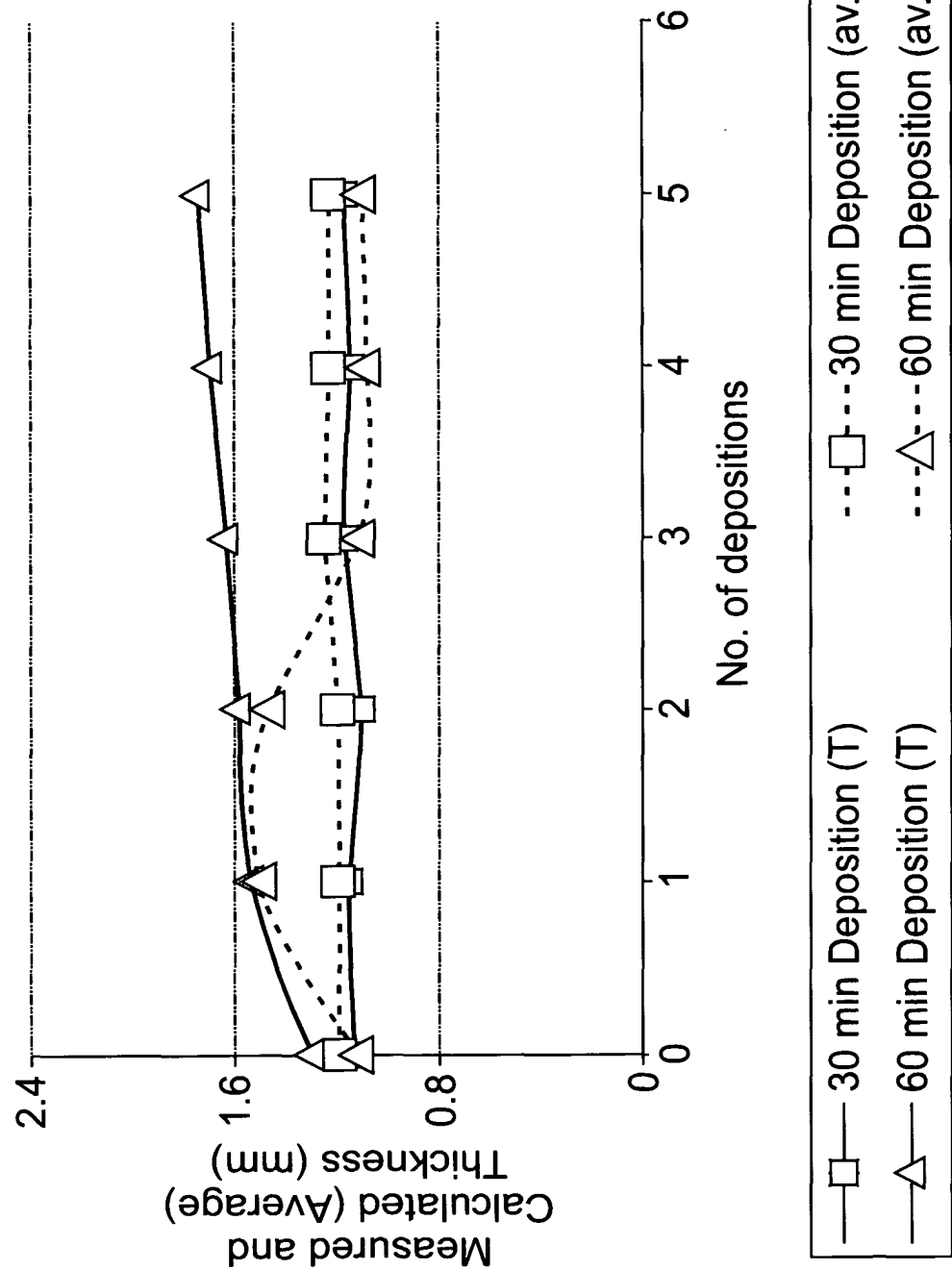


Fig. 4

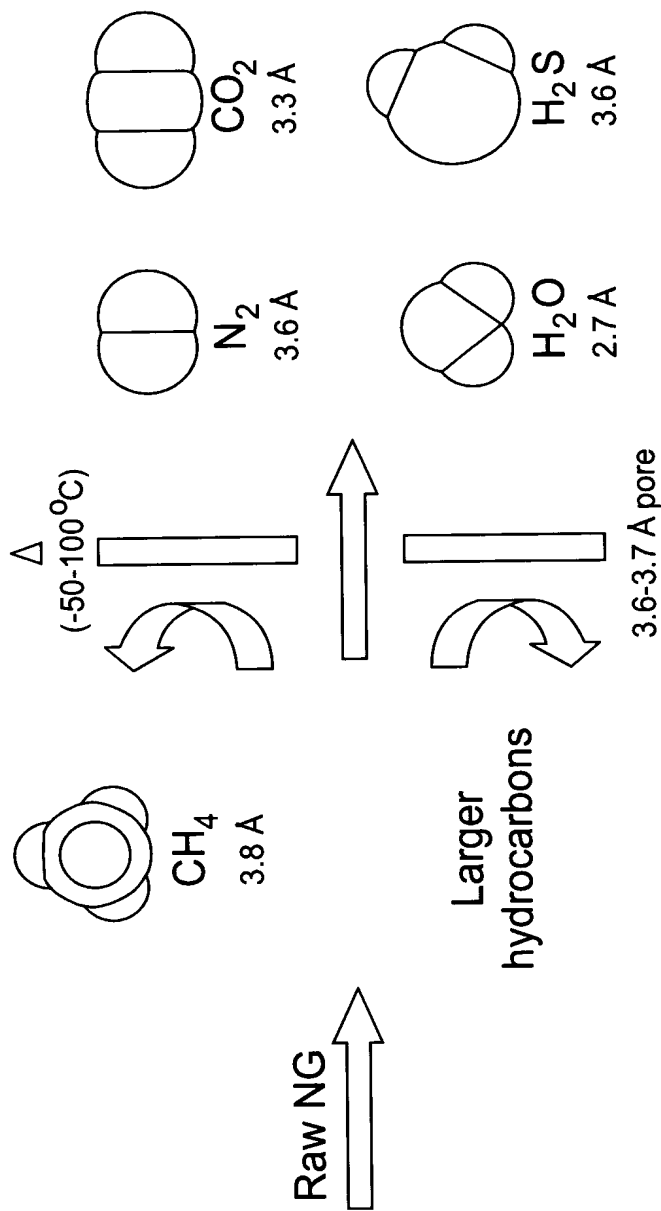
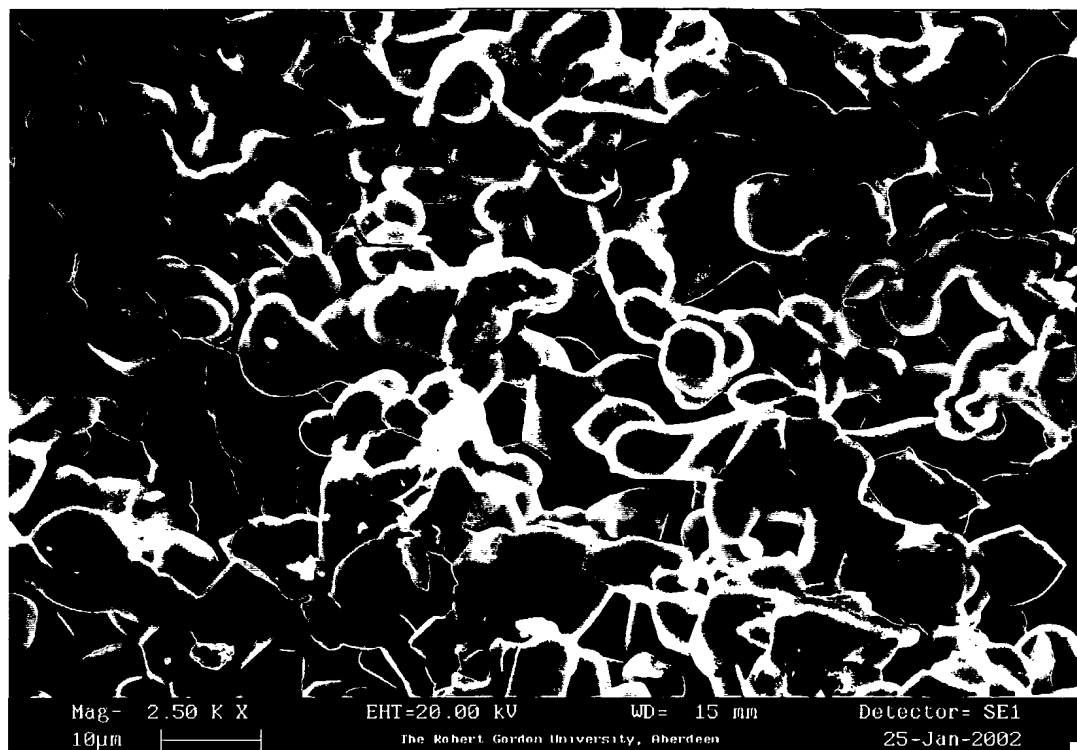
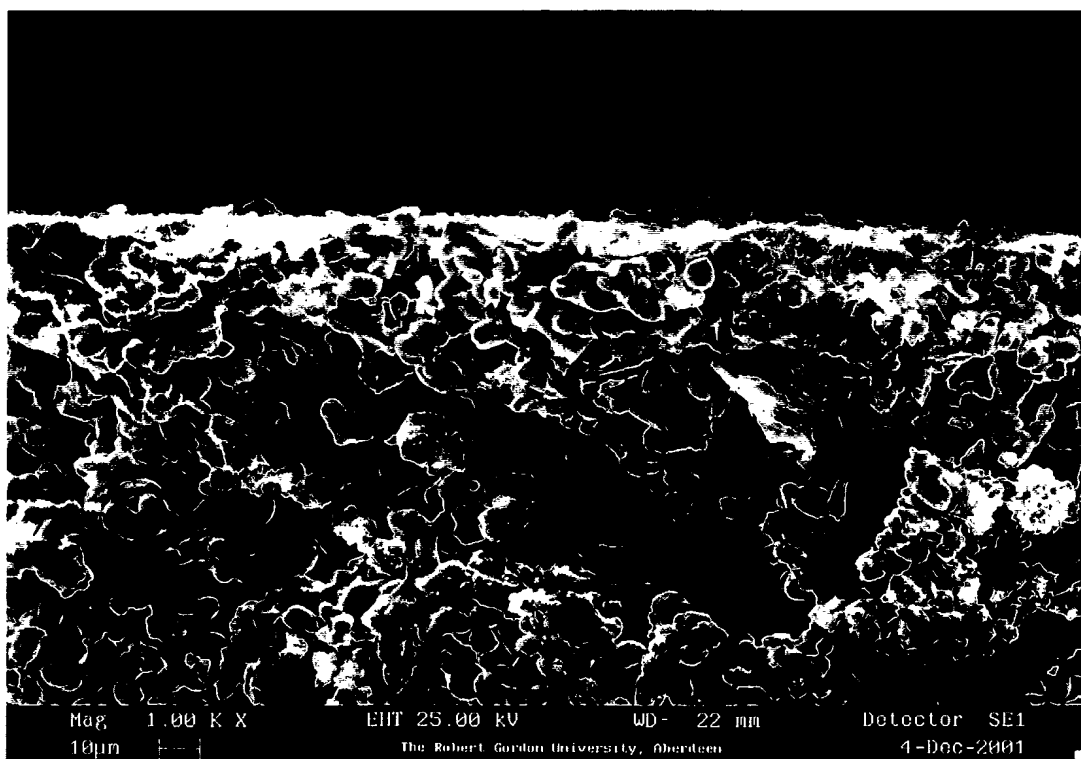


Fig. 5

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*Fig. 6a**Fig. 6b*

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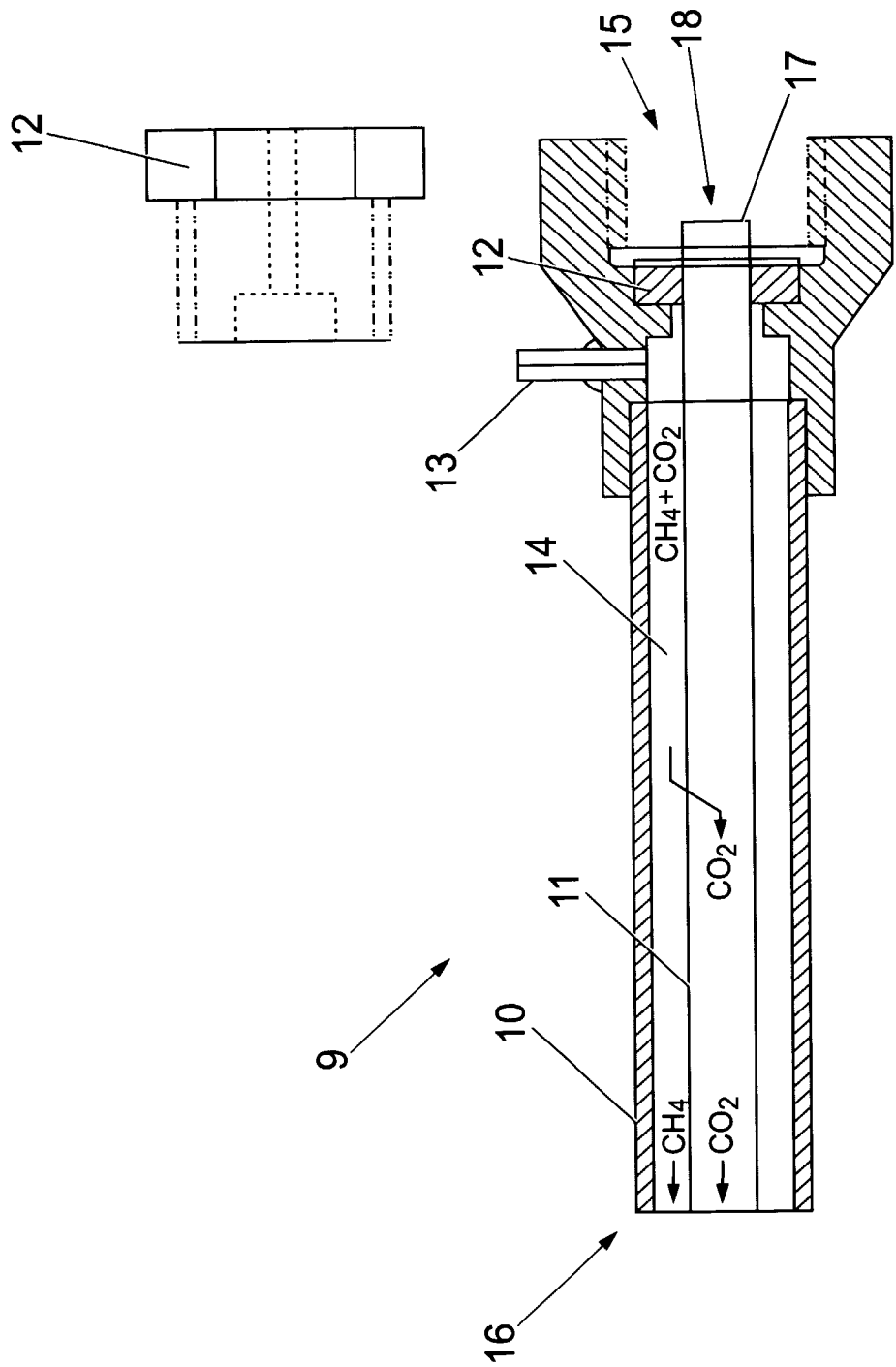


Fig. 7

INTERNATIONAL SEARCH REPORT

International Application No

PC/GB 02/01079

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/22 B01D71/02 B01D63/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Week 200111 Derwent Publications Ltd., London, GB; AN 2001-097914 XP002203448 & JP 2000 334250 A (KYOCERA CORP), 5 December 2000 (2000-12-05) abstract</p>	1,2
X	<p>DATABASE WPI Week 199621 Derwent Publications Ltd., London, GB; AN 1996-203628 XP002203449 & JP 08 071386 A (KYOCERA CORP), 19 March 1996 (1996-03-19) abstract</p>	1,2,4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

25 June 2002

Date of mailing of the international search report

08/07/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cordero Alvarez, M

INTERNATIONAL SEARCH REPORT

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 06, 30 April 1998 (1998-04-30) & JP 10 052629 A (KANEBO LTD), 24 February 1998 (1998-02-24) abstract ---	1,2,9,10
X	US 6 152 986 A (P.C.FOLLER) 28 November 2000 (2000-11-28) claim 1 ---	25-28
X,P	DATABASE WPI Week 200219 Derwent Publications Ltd., London, GB; AN 2002-143369 XP002203450 & JP 2001 276586 A (KYOCERA CORP), 9 October 2001 (2001-10-09) abstract ---	1,2,19, 20
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 04, 30 April 1996 (1996-04-30) & JP 07 313853 A (NOK CORP), 5 December 1995 (1995-12-05) abstract ---	2,9,14, 15
A	PATENT ABSTRACTS OF JAPAN vol. 0050, no. 08 (C-039), 20 January 1981 (1981-01-20) & JP 55 137209 A (MITSUBISHI RAYON CO LTD), 25 October 1980 (1980-10-25) abstract ---	1,2,9, 16-18
A	PATENT ABSTRACTS OF JAPAN vol. 0173, no. 67 (C-1082), 12 July 1993 (1993-07-12) & JP 05 057162 A (NOK CORP), 9 March 1993 (1993-03-09) abstract ---	14-16,19
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 11, 28 November 1997 (1997-11-28) & JP 09 173798 A (KYOCERA CORP), 8 July 1997 (1997-07-08) abstract -----	2,9,14, 15

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/01079

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2000334250	A	05-12-2000	NONE	
JP 8071386	A	19-03-1996	NONE	
JP 10052629	A	24-02-1998	NONE	
US 6152986	A	28-11-2000	AU 5921100 A WO 0102290 A1	22-01-2001 11-01-2001
JP 2001276586	A	09-10-2001	NONE	
JP 07313853	A	05-12-1995	NONE	
JP 55137209	A	25-10-1980	JP 1380200 C JP 61049405 B	28-05-1987 29-10-1986
JP 05057162	A	09-03-1993	NONE	
JP 09173798	A	08-07-1997	NONE	